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Transport Processes Involving Organic Chemicals

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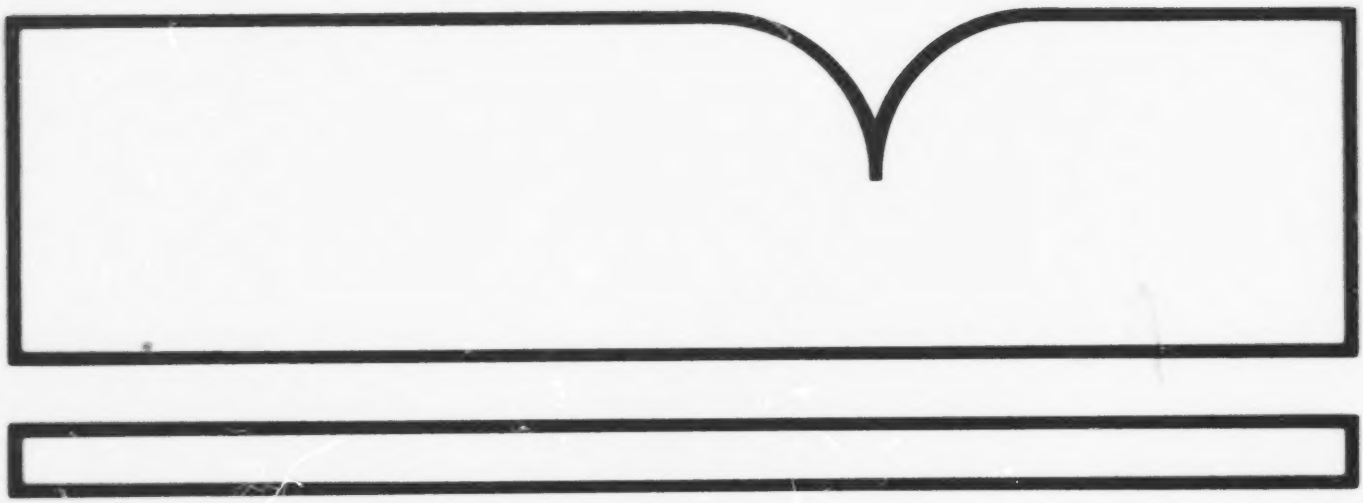

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16. ABSTRACT

Groundwater use in the USA has more than doubled between 1950 and 1975, and more than 40% of the USA population utilizes groundwater as a drinking water source. These figures, coupled with the enormous cost of groundwater remediation, underscore the importance of understanding chemical transport through soil and in groundwater. This document discusses three aspects of organic chemical transport. The first topic of discussion describes how cationic surfactants can effectively increase the organic carbon content, and thus the sorption capacity, of geologic material. Conversely, if a mobile hydrophobic phase is present, such as colloidal sized organic particles dispersed in the aqueous phase, chemical transport may be greatly facilitated through sorption on the mobile organic phase. This is the second topic of discussion. The third and final topic of discussion is chemical transport in the presence of residual hydrocarbons resulting from the entrapment of hydrocarbonaceous fluids, such as petroleum derived fuels and solvents, in the pore space of geologic material.

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14 Transport Processes Involving Organic Chemicals[1]

D. C. Bouchard, C. G. Enfield, and M. D. Piwoni

USEPA
Ada, Oklahoma

As man has continuously sought to improve his environment, his efforts have evolved to the synthesis of organic compounds used in the myriad of products essential to life as we know it. There is no turning back to a whimsical, simpler time of a universally pure environment. Today we must make tough decisions on environmental questions: which compounds are safe, what is an acceptable level of risk, when is a benefit worth the cost? To answer these questions intelligently, we must have an understanding of the fate of man-made organic compounds in the environment.

Understanding organic chemical transport through soil and subsurface geologic material is requisite for making intelligent decisions on hazardous waste disposal and on the remedial actions necessary when hazardous wastes are disposed of improperly. Groundwater use in the USA more than doubled between 1950 and 1975 (Burmaster & Harris, 1982). In addition, more than 40% of the U.S. population utilizes groundwater as a drinking water source, and 25% of all fresh-water use in the USA is groundwater (McCarty et al., 1981). These figures, coupled with the enormous cost of groundwater remediation, underscore the importance of understanding all of the phenomena that can affect organic chemical transport through soil and other geologic material to groundwater.

The transport of organic chemicals through geologic material is governed by many physical, chemical, and biological processes. Transport of neutral organic compounds (NOCs) has usually been described utilizing theories and conceptualizations developed for liquid chromatography. In these models, it is assumed that the concentration of a chemical in solution is low relative to its solubility, that chemicals in solution act independently of each other, and that sorption is driven by the favorable thermodynamics of solute removal from solution through sorption on a stationary and unchanging hydrophobic phase (Horvath et al., 1976). See Rao and Jessup (1983), and Boesten and Leistra (1983) for reviews of mathematical models used to describe the

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effects of advection, dispersion, sorption, and transformation on solute transport through geologic material. The degree of organic chemical sorption, and therefore the retardation relative to the movement of water, is a function of solute hydrophobicity and the amount of sorbent hydrophobic phase. Properties that reflect chemical hydrophobicity, such as aqueous solubility, octanol-water partition coefficient (K_{ow}), and reverse-phase chromatographic retention time, have been successfully used to predict sorption (Carlson et al., 1975; Kenaga & Goring, 1980; Karickhoff, 1981; Brown & Flagg, 1981; Weber et al., 1986; Chin et al., 1986). In addition, the importance of soil organic C as a hydrophobic sorbing surface has been repeatedly demonstrated (Karickhoff et al., 1979; Chiou et al., 1983).

Given the importance of hydrophobic interactions in determining the transport of NOCs in the environment, it is apparent that any perturbation of the amount of hydrophobic phase present in a system will dramatically affect NOCs transport. If the hydrophobic phase considered is stationary, as is the case for natural organic C associated with geologic material, then an increase in the organic C content of the geologic material will result in increased NOCs sorption on that material. The first topic of discussion describes how cationic surfactants can effectively increase the organic C content, and thus the sorptivity for NOCs, of geologic material. Conversely, if a mobile hydrophobic phase is present, such as colloidal-sized organic particles dispersed in the aqueous phase, NOCs transport may be greatly facilitated through sorption on this mobile organic phase. This is the second topic of discussion.

The third and final topic of discussion is the organic phase, commonly called the residual saturation, remaining behind after a water immiscible fluid, such as gasoline, has passed through geologic material. The residual saturation of a hydrocarbon fluid may be conceptualized as a stationary organic C phase that is continuously becoming more hydrophobic and resistant to aqueous phase transport as the volatile and water soluble components are weathered from the phase. Aspects of residual saturation as an immobile hydrophobic phase that effectively increases the sorptivity of geologic materials for NOCs are discussed.

14–1 ORGANIC CATION EFFECTS ON THE TRANSPORT OF METALS AND NEUTRAL ORGANIC COMPOUNDS

To understand organic cation effects on sorbent sorptivity, it is first necessary to understand the interaction between organic cations and geologic material. Retention of NOCs is primarily dependent on the NOCs' solubility and sorbent's organic C content. Retention of cationic organic compounds, on the other hand, is dependent on solute solubility and sorbent cation exchange capacity (CEC) in addition to the sorbent's organic C. Even though sorbent organic C content directly influences CEC, subsurface materials low in organic C can still possess significant CEC arising from the permanent and pH dependent exchange sites on clay minerals. Figure 14–1

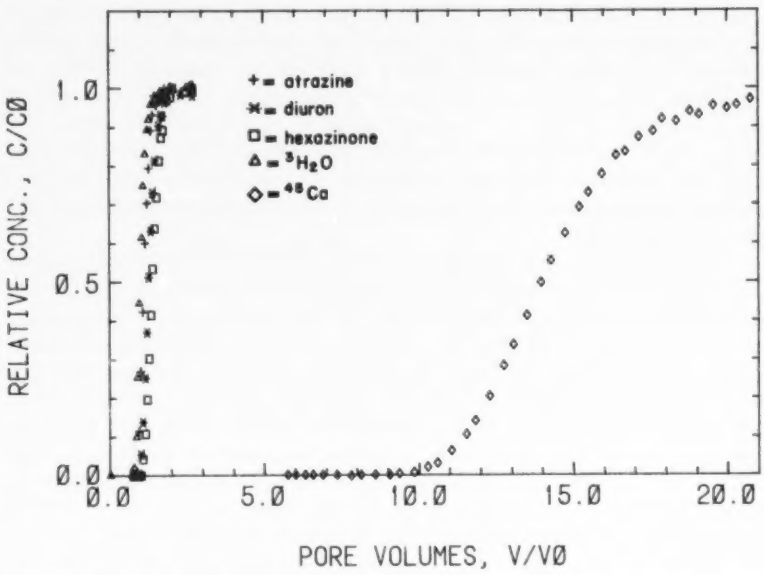

Fig. 14-1. The BTCs of ^3H_2O, three herbicides, and ^{45}Ca on low organic C (0.3 g kg^{-1}) saturated zone material (Bouchard et al., 1988a).

shows the breakthrough curves (BTCs) for ^{45}Ca, ^3H_2O, and three NOCs, in this case three herbicides, through a low organic C (0.3 g kg^{-1}) material from the saturated zone. It is clear that this material has much more capacity to retard the movement of cations than these neutral organic compounds. Low organic C subsurface materials that have little sorptivity for NOCs may, nevertheless, interact strongly with organic cations.

Alkylammonium cations and clay minerals have been the most widely used materials for elucidating organic cation–geologic material interactions (McBride & Mortland, 1975; McBride et al., 1977; Stul et al., 1979; Stul & De Bock, 1985). These studies have shown that organic cations are strongly retained on clay minerals. The term *sorption* is appropriately applied to the organic cation retention mechanism because organic cation retention on geologic material is due to both site specific electrostatic interactions (adsorption) and nonspecific hydrophobic effects due to the hydrocarbon moiety's low solubility in water (partitioning or absorption). As the organic cation hydrocarbon moiety increases in size, hydrophobic effects increase in importance. Evidence for hydrophobic effects in organic cation sorption is that organic cations may be sorbed in excess of sorbent CEC (Malik et al., 1972; Wolfe et al., 1985), and that organic cation sorption on montmorillonite increased with the size of the organic cation hydrocarbon moiety (Malik et al., 1972; Sarkar & Das Kanungo, 1983).

Since large organic cations are sorbed due to both electrostatic and hydrophobic effects, organic cations will be less mobile in geologic material

than would be predicted on the basis of electrostatic or hydrophobic retention mechanisms alone. For large organic cations sorption is strong and essentially irreversible. Two important consequences of the high sorption of organic cations are increased metals mobility as organic cations replace metals on the exchange complex of geologic material, and a profound change in the sorptivity of geologic materials for NOCs following organic cation sorption. The focus of this discussion is on the later phenomenon, but for purposes of completeness a brief discussion of organic cation effects on metals transport follows.

Sorption of organic cations with large hydrocarbon moieties has been observed to be accompanied by a near equimolar desorption of metals from the exchange complex of geologic materials (Bouchard et al., 1988). Sarkar and Das Kanungo (1983) observed that organic cation replaceability of metals increased as organic cation solubility decreased due to increases in alkyl chain length. Since large organic cations have surfactant properties, it is appropriate to compare the effects of these organic cations on metals transport with the effects of anionic and nonionic surfactants. Generally, nonionic surfactants have little effect on metals transport. Anionic surfactants, however, may increase or decrease metals mobility depending on the organic anion–metal complex aqueous solubility (Beveridge & Pickering, 1983).

Organic cation effects on geologic material sorptivity are important because the organic C content of most subsurface geologic material is much lower than that of surface soil, and as a result the sorptivity of subsurface material from the vadose and saturated zone for NOCs is low (Schwarzenbach & Westall, 1981; Banerjee et al., 1985; Bouchard et al., 1988a). Figure 14–2 shows the BTCs for ^3H_2O and three herbicides through saturated zone material with an organic C content of 0.3 g kg^{-1}. The low sorptivity of the subsurface material is reflected in retardation factors <1.5 for the three herbicides.

Some noncarbon based sorption of polar NOCs has been observed on very low organic C (generally <1.0 g kg^{-1}) geologic materials (Hassett et al., 1980; Banerjee et al., 1985; Bouchard & Wood, 1988). In these studies, increases in the C normalized sorption coefficient (K_{oc}) were observed with decreases in the sorbent organic C content, indicating that noncarbon, or mineral surfaces, contributions to sorptivity were measurable at low organic C content. Evidence for noncarbon based sorption is contained in Fig. 14–2 where the herbicide hexazinone was more highly retarded than two other herbicides with water solubilities three orders of magnitude lower. For compounds, like hexazinone, that contain polar functionalities capable of site specific interactions (adsorption) some noncarbon based sorption may occur. Generally, however, it can be expected that all but the very hydrophobic NOCs will be very slightly sorbed on low organic C geologic materials.

Low NOCs sorption on saturated zone material is desirable from the standpoint of groundwater remediation in that solute removal by pumping to the surface is facilitated. However, the problems of contaminant migration control are exacerbated when the contaminants move essentially unsorbed at a velocity near that of water. Contaminant migration control then becomes

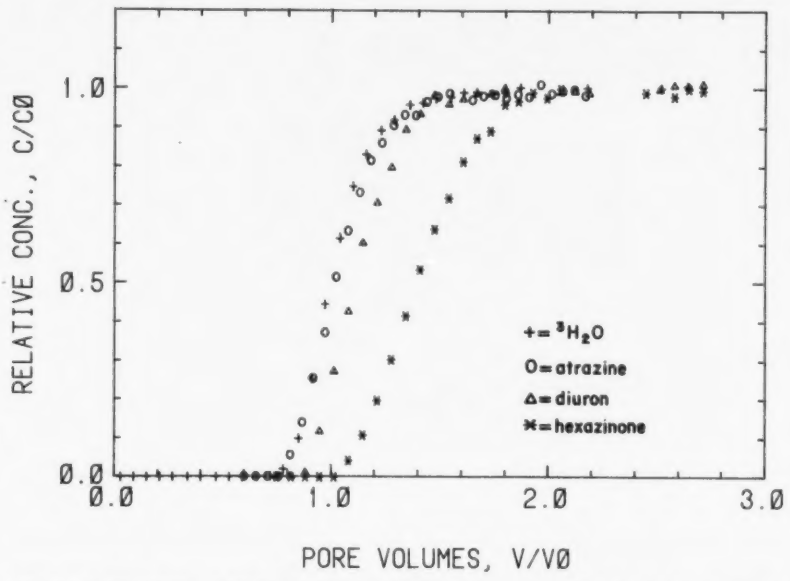

Fig. 14–2. The BTCs of ^3H_2O and three herbicides on low organic C (0.3 g kg^{-1}) saturated zone material (Bouchard & Wood, 1988).

a function of hydrologic control and is usually effected with clay caps and clay liners of low hydraulic conductivity.

Clay minerals without associated organic C display low sorptivity for many organic contaminants, so permeability to water through a clay barrier may, also, result in permeability to contaminants. In addition, contaminant migration control through reduction of site permeability is not compatible with chemical and biological in situ remediation technologies that rely upon reagent transport in the aqueous phase to contaminated zones. For these technologies, it is necessary to keep the contaminants within the treatment zone long enough to effect successful transformation to innocuous products. For both clay barriers and in situ remediation, one way to slow contaminant transport is to increase contaminant sorption on geologic material. The effects of organic cations on the sorptivity of geologic material, primarily montmorillonite, have been studied for the past 40 yr (Jordan, 1949; Barrer & MacLeod, 1955). Recently, however, there has been a rekindling of interest in the use of organic cations as sorptivity enhancers of geologic material to effect solute migration control and mitigate contaminant dispersal in the environment (Wolfe et al., 1985; Mortland et al., 1986; Bouchard et al., 1988).

Figure 14–3 is a schematic representation of a clay mineral surface and illustrates why NOCs sorption on clay mineral surfaces is minimal. Due primarily to substitution of lower valent metals in the crystal lattice, some clay minerals possess a net negative charge that exists in association with a suite of metal counterions to maintain overall charge neutrality. The result

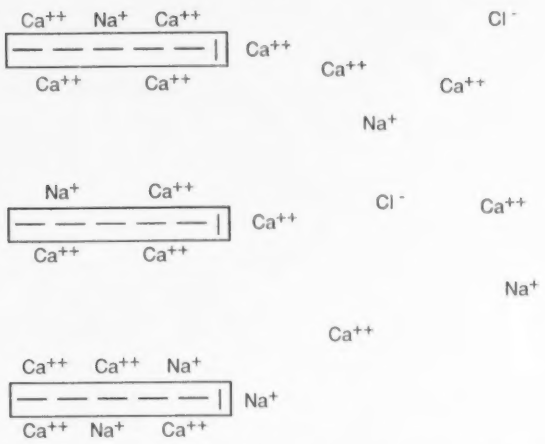

Fig. 14-3. Schematic representation of a laminar clay mineral and associated metal counterions.

is a very hydrophilic surface where nonpolar and weakly polar NOCs are unable to displace metals or their hydration spheres due to the relative weakness of their interactions with the mineral surface or adsorbed metals. The NOCs coordination with adsorbed transition metals may occur in the absence of water (Doner & Mortland, 1969; Mortland & Pinnavaia, 1971) but retention by this mechanism is probably insignificant in an aqueous environment. When organic cations replace metals on the mineral surface exchange complex (Fig. 14-4), the mineral surface is transformed from hydrophilic to hydrophobic by the presence of the hydrocarbon moiety of the sorbed organic cations (Jordan, 1949; Lagaly, 1984). The result can be a great increase in mineral surface sorptivity for NOCs.

Figure 14-5 shows the increase in toluene sorption on a low organic C saturated zone material resulting from sorption of the organic cation ethylhexadecyldimethylammonium (EHDDMA+). Mortland et al. (1986) observed that solute sorption on an organic cation-smectite complex increased with solute hydrophobicity for chlorinated phenols, which indicated the existence of a hydrophobic surface. Organic cations with large hydrophobic moieties, like EHDDMA+, are better sorption enhancers than small organic cations as the large organic cations are themselves more strongly sorbed and provide more hydrophobic surface per mole when sorbed to geologic material.

The organic C of the EHDDMA+ alkyl moiety was more efficient than the natural organic C of the saturated zone material in sorbing toluene from aqueous solution. Boyd et al. (1987) also found organic cation-smectite complexes to be an order of magnitude more efficient than natural organic C in sorbing benzene and pentachlorophenol from aqueous solution. The high sorptivity of the organic cation-mineral complexes may be explained by the nature of the organic C of the sorbed organic cations. With no polar func-

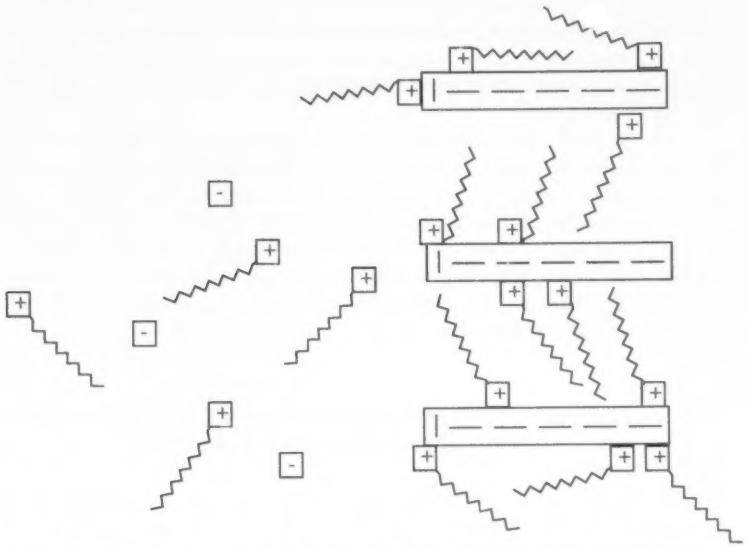

Fig. 14-4. Schematic representation of a laminar clay mineral and sorbed organic cations.

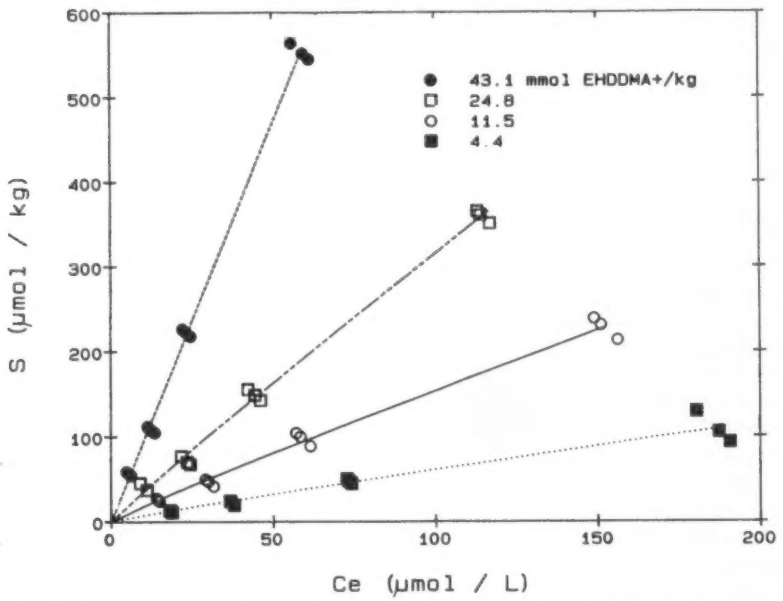

Fig. 14-5. Toluene sorption isotherms at varying EHDDMA+ sorbed phase concentrations (Bouchard et al., 1988).

tional groups to mitigate hydrophobicity, the alkyl chains of the sorbed organic cations constitute a more hydrophobic environment than natural organic C. Garbarini and Lion (1986) observed that the hydrophobic fats-waxes-resins extract of a soil yielded sorption coefficients 50 times greater than the whole soil.

To conclude, the sorption of NOCs can be greatly increased through the cosorption of large, surfactant type organic cations. The consequence of this increased sorption is, of course, decreased NOCs mobility. At low organic cation concentrations, the added sorptivity to soils or geologic materials high in natural organic C may be insignificant. However, on very low organic C sorbents, such as many subsurface geologic materials, small additions to sorptivity will be very significant and organic cations will have a large impact on the transport of neutral organic compounds.

14–2 SOLUTE TRANSPORT IN ASSOCIATION WITH DISPERSED COLLOIDAL MATTER

In a simple system consisting of a solute and stationary geologic material as the sorbent, solute transport will be governed by solute sorption on the organic C or mineral phase of the geologic material and the convective-dispersive processes affecting aqueous phase transport. In this system, the solute can exist in two phases, solution (mobile) and sorbed (immobile). Because of their high degree of sorption on geologic material, solutes such as many radionuclides and low solubility organic compounds are considered to be immobile in the environment and therefore not potential contaminants of groundwater. However, simple systems are rarely encountered in nature, and the following discussion addresses more complex systems where colloidal material is dispersed in the aqueous phase.

When colloidal material is present in the aqueous phase as a result of unsettled soil particles following agitation (Voice et al., 1983; Gschwend & Wu, 1985), or as colloidal organic material (Wershaw et al., 1969; Ballard, 1971; Poirrier et al., 1972; Boehm & Quinn, 1973), a three phase system exists where the solute may be sorbed to the stationary geologic material or to dispersed colloidal material, or be in solution. Solute transport is then governed by the velocity and sorptivity of the mobile colloidal phase in addition to pore water velocity and sorption on geologic material. If hazardous chemicals sorb to the colloidal material, current solute transport models that assume partitioning between a mobile aqueous phase and a stationary organic C or mineral phase may significantly underestimate contaminant mobility, and result in underestimation of environmental exposure and risk.

Solute sorption on colloidal material dispersed in the aqueous phase is a function of both solute and colloid characteristics, and results in an increase in the apparent solubility of the solute. Transport of the colloid-solute specie in the environment will depend on the convective transport of the aqueous phase and the degree of colloid association with stationary geologic material.

Much of the research on association of inorganic solutes with colloidal material has been studies in radionuclide distribution between aqueous and solid phases. The apparent solubility of many radionuclides is enhanced through complexation with naturally occurring humic and fulvic acids, or through electrostatic binding to colloidal clay, metal oxides, or other inorganic colloids. The importance of colloidal organic C (COC) in determining the distribution of actinide elements in several North American lakes has been documented (Nelson et al., 1985). Means et al. (1978) found that 30% of the U and up to 10% of the ^{60}Co in groundwater near a radioactive waste disposal site were associated with COC. While metals distribution has often been correlated with COC, the polyelectrolytic nature of COC has hindered development of a general complexation model for metals and COC (Perdue & Lytle, 1983).

Inorganic colloids are also important in radionuclide distribution. Actinide elements may associate with colloidal Fe oxides (Nakayama et al., 1986) or other inorganic colloids in groundwater (Kim et al., 1984). Buddemeier (1986) reported that most of the radionuclides detected outside of a nuclear test zone were associated with colloids >0.6 nm in diam. and that this colloidal fraction contained clay minerals. In addition to inorganic colloidal material originating from natural geologic material, inorganic colloids may be formed in situ as a result of the introduction of anthropogenic chemicals. Colloidal ferrous phosphate particles were formed in situ in an Fe-rich aquifer on Cape Cod as a result of the presence of phosphate containing surfactants (Gschwend & Reynolds, 1987).

For most NOCs, hydrophobic sorption on organic colloids is a much more important solubilizing process than NOCs associated with inorganic colloids. This is due to basic differences in sorptivity for NOCs of organic and mineral surfaces. Organic colloids, either in solution or present as coatings on mineral particles, provide a hydrophobic microenvironment not present on hydrophilic mineral surfaces that allows NOCs partitioning out of the aqueous phase.

The source of COC may be anthropogenic as in landfill leachate or effluents from industrial processes; or naturally occurring such as humic and fulvic acids. The COC concentration range in groundwater resulting from man's activities is limited only by the source concentration and the organic C aqueous solubility. Common levels of naturally occurring COC in groundwaters range from 0.5–0.7 mg L^{-1} in igneous, sand, or gravel aquifers, to 3–10 mg L^{-1} in oil shales and humic colored groundwaters (Thurman, 1985).

The NOCs sorption to COC and an increase in apparent NOCs solution concentration has been observed in numerous studies (Carter & Suffet, 1982; Hassett & Anderson, 1982; Perdue & Lytle, 1983; Carlson et al., 1985; McCarthy & Jimenez, 1985; Caron et al., 1985). Enfield et al. (1982) proposed NOCs sorption and transport on COC as an explanation for why hydrophobic compounds, like the pesticide DDT (dichlorodiphenyl trichloroethane), have been observed to be much more mobile in the environment than predicted by models that assumed a simple two phase system consisting

of an aqueous (mobile) and sorbed (immobile) phase. More recently, further work has suggested that macromolecules or water immiscible phases transported in the aqueous phase may facilitate NOCs transport (Enfield, 1985).

The COC effects on the apparent solubility of NOCs is most significant for low solubility, highly sorbed, solutes. It is for these hydrophobic NOCs that the relative increases in solubility due to sorption on colloidal material is the greatest. Also, since NOCs apparent solubility is dependent on hydrophobic sorption to COC, NOCs apparent solubility will increase with COC concentration. Bengtsson et al. (1987) observed an increase in hexachlorobenzene apparent solubility with increasing organic colloid concentration. Chiou et al. (1986) observed that the apparent solubility of DDT and polychlorinated biphenyls (PCBs) increased linearly with organic colloid concentration.

It has been observed that the concentration and chemical composition of COC may vary considerably in natural waters from different geographic locations, and that structural differences in similar macromolecules may result in order of magnitude or greater differences in sorptivity for NOCs (Landrum et al., 1984; Whitehouse, 1985; Gauthier et al., 1987). Small, polar, molecules may not provide an adequate hydrophobic environment to allow NOCs partitioning out of the aqueous phase. However, large macromolecules with nonpolar moieties would provide the necessary hydrophobic microenvironment to allow NOCs partitioning from solution. Research has shown that COC does differ in its ability to sorb NOCs, and that COC sorptivity increases with COC size and hydrophobicity (Chiou et al., 1986). Also, humic and fulvic acids comprise 20 to 60% of groundwater COC (Thurman, 1985; Collins et al., 1986), and the higher carbon to oxygen (C/O) ratio of groundwater than surface water humic material (Thurman, 1985) suggests a greater hydrophobicity and therefore greater sorptivity for NOCs by groundwater humic material.

Once NOCs concentration in the aqueous phase has been increased through sorption on COC, the COC itself must be mobile in groundwater to facilitate NOCs transport. Robertson et al. (1984) observed that COC waste from paper manufacturing was as mobile as Na ions in a sandy aquifer. Also, Nightengale and Bianchi (1977) observed colloidal clay transport from surface soils to wells several hundred meters from the recharge zone. Anionic surfactants have moved as conservative tracers in groundwater (Thurman, 1985). Enfield and Bengtsson (1988) reported that the macromolecule blue dextran was transported more rapidly than ^3H_2O through a soil column (Fig. 14–6). The authors explained the rapid dextran transport as being analogous to size exclusion chromatography where the large dextran molecule was excluded from small pores that were accessible to water. These observations of high colloid mobility coupled with hydrophobic NOCs sorption to COC indicate the potential importance of COC as a mobile organic C phase that can facilitate the transport of hydrophobic NOCs that would be very immobile in a two phase system.

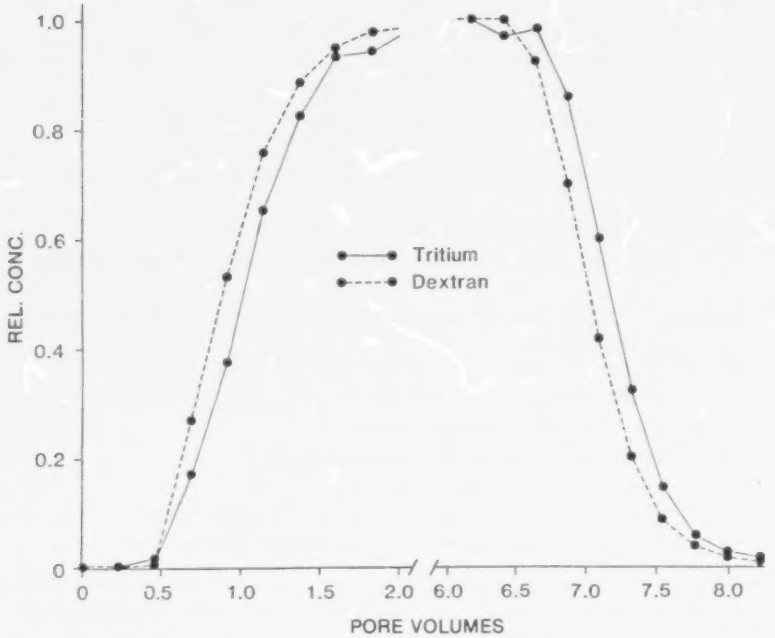

Fig. 14–6. The BTCs of ^3H_2O and the dextran macromolecule on a sandy surface soil (Enfield & Bengtsson, 1988).

Enfield and Bengtsson (1988) have proposed describing the colloid facilitated transport discussed previously by dividing a representative elemental volume of the soil system into three phases: a liquid or aqueous phase; a solid phase, the soil; and a mobile organic phase, the macromolecule. The following equations were written to describe the individual phases

$$\frac{\partial(\theta\rho_a C_a)}{\partial t} = D_a \frac{\partial^2(\theta\rho_a C_a)}{\partial x^2} - V_a \frac{\partial(\theta\rho_a C_a)}{\partial x} - K_{ao}\theta\rho_a C_a + K_{oa}\phi\rho_o C_o - K_{as}\theta\rho_a C_a + K_{sa}(1 - n)\rho_s C_s \quad [1]$$

$$\frac{\partial[(1 - n)\rho_s C_s]}{\partial t} = -K_{sa}(1 - n)\rho_s C_s + K_{as}\theta\rho_a C_a \quad [2]$$

$$\frac{\partial(\phi\rho_o C_o)}{\partial t} = D_o \frac{\partial^2(\phi\rho_o C_o)}{\partial x^2} - V_o \frac{\partial(\phi\rho_o C_o)}{\partial x} - K_{oa}\phi\rho_o C_o + K_{ao}\theta\rho_a C_a \quad [3]$$

where

C_a = concentration in aqueous phase, kg kg^{-1}
C_o = concentration in mobile organic phase, kg kg^{-1}
C_s = concentration in solid phase, kg kg^{-1}
D_a = dispersion in aqueous phase, m^2 d^{-1}
D_o = dispersion in mobile organic phase, m^2 d^{-1}
K_{ao} = first order transfer coefficient aqueous to mobile organic phase, d^{-1}
K_{as} = first order transfer coefficient aqueous to solid phase, d^{-1}
K_{oa} = first order transfer coefficient mobile organic to aqueous phase, d^{-1}
K_{sa} = first order transfer coefficient solid to aqueous phase, d^{-1}
n = porosity of the soil, m^3 m^{-3}
V_a = interstitial velocity of aqueous phase, m d^{-1}
V_o = interstitial velocity of mobile organic phase, m d^{-1}
ρ_a = density of aqueous phase, Mg m^{-3}
ρ_o = density of mobile organic phase, Mg m^{-3}
ρ_s = particle density of the soil, Mg m^{-3}
ϕ = volume fraction occupied by the mobile organic phase
θ = volume fraction occupied by the aqueous phase

In writing the previous equations, the aqueous phase was assumed to totally cover both the solid phase and the mobile organic phase or macromolecule such that transfer of the contaminant from the mobile organic phase to the solid phase requires passage through the aqueous phase. The total change in an elemental volume can be written as the sum of Eq. [1] through [3] or

$$\frac{\partial(\theta\rho_a C_a)}{\partial t} + \frac{\partial(\phi\rho_o C_o)}{\partial t} + \frac{\partial[(1 - n)\rho_s C_s]}{\partial t}$$

$$= D_a \frac{\partial^2(\theta\rho_a C_a)}{\partial x^2} + D_o \frac{\partial^2(\phi\rho_o C_o)}{\partial x^2} - V_a \frac{\partial(\theta\rho_a C_a)}{\partial x} - V_o \frac{\partial(\phi\rho_o C_o)}{\partial x}. \quad [4]$$

When local equilibrium exists

$$K_{ao}\theta\rho_a C_a = K_{oa}\phi\rho_o C_o \quad [5]$$

or

$$K_p = \frac{K_{ao}\theta\rho_a}{K_{oa}\phi\rho_o} = \frac{C_o}{C_a}$$

and

$$K_{as}\theta\rho_a C_a = K_{sa}[(1 - n)\rho_s C_s \quad [6]$$

where

C_a = concentration in aqueous phase, kg kg^{-1}
C_o = concentration in mobile organic phase, kg kg^{-1}
C_s = concentration in solid phase, kg kg^{-1}
D_a = dispersion in aqueous phase, m^2 d^{-1}
D_o = dispersion in mobile organic phase, m^2 d^{-1}
K_{ao} = first order transfer coefficient aqueous to mobile organic phase, d^{-1}
K_{as} = first order transfer coefficient aqueous to solid phase, d^{-1}
K_{oa} = first order transfer coefficient mobile organic to aqueous phase, d^{-1}
K_{sa} = first order transfer coefficient solid to aqueous phase, d^{-1}
n = porosity of the soil, m^3 m^{-3}
V_a = interstitial velocity of aqueous phase, m d^{-1}
V_o = interstitial velocity of mobile organic phase, m d^{-1}
ρ_a = density of aqueous phase, Mg m^{-3}
ρ_o = density of mobile organic phase, Mg m^{-3}
ρ_s = particle density of the soil, Mg m^{-3}
ϕ = volume fraction occupied by the mobile organic phase
θ = volume fraction occupied by the aqueous phase

In writing the previous equations, the aqueous phase was assumed to totally cover both the solid phase and the mobile organic phase or macromolecule such that transfer of the contaminant from the mobile organic phase to the solid phase requires passage through the aqueous phase. The total change in an elemental volume can be written as the sum of Eq. [1] through [3] or

$$\frac{\partial(\theta\rho_a C_a)}{\partial t} + \frac{\partial(\phi\rho_o C_o)}{\partial t} + \frac{\partial[(1 - n)\rho_s C_s]}{\partial t}$$

$$= D_a \frac{\partial^2(\theta\rho_a C_a)}{\partial x^2} + D_o \frac{\partial^2(\phi\rho_o C_o)}{\partial x^2} - V_a \frac{\partial(\theta\rho_a C_a)}{\partial x} - V_o \frac{\partial(\phi\rho_o C_o)}{\partial x}. \quad [4]$$

When local equilibrium exists

$$K_{ao}\theta\rho_a C_a = K_{oa}\phi\rho_o C_o \quad [5]$$

or

$$K_p = \frac{K_{ao}\theta\rho_a}{K_{oa}\phi\rho_o} = \frac{C_o}{C_a}$$

and

$$K_{as}\theta\rho_a C_a = K_{sa}[(1 - n)\rho_s C_s \quad [6]$$

or

$$K_d = \frac{K_{as}\theta\rho_a}{K_{sa}(1 - n)\rho_s} = \frac{C_s}{C_a}.$$

Defining a new variable C^* as the total mass concentration of the mobile contaminant over all phases

$$C^* = \theta\rho_a C_a + \phi\rho_o C_o \quad [7]$$

then the total change in the elemental volume can be shown to follow the equation

$$\left(1 + \frac{K_{ao}}{K_{oa}} + \frac{K_{as}}{K_{sa}}\right)\frac{\partial C^*}{\partial t} = \left(D_a + \frac{K_{ao}}{K_{oa}} D_o\right)\frac{\partial^2 C^*}{\partial x^2} - \left(V_a + \frac{K_{ao}}{K_{oa}} V_o\right)\frac{\partial C^*}{\partial x}. \quad [8]$$

By defining the variables

$$R^* = 1 + \frac{K_{ao}}{K_{oa}} + \frac{K_{as}}{K_{sa}} \quad [9]$$

$$D^* = D_a + \frac{K_{ao}}{K_{oa}} D_o \quad [10]$$

and

$$V^* = V_a + \frac{K_{ao}}{K_{oa}} V_o \quad [11]$$

Equation [8] becomes

$$R^*\frac{\partial C^*}{\partial t} = D^*\frac{\partial^2 C^*}{\partial x^2} - V^*\frac{\partial C^*}{\partial x}. \quad [12]$$

Equation [12] has been solved for a variety of boundary conditions. Several solutions have been summarized by van Genuchten and Alves (1982).

Two theoretical figures were developed by Enfield and Bengtsson (1988) to demonstrate the significance of the presence of the macromolecule and the differences in interstitial velocities between fluid phases for the transport of trace organic pollutants. Several simplifying assumptions were made in

the development of the figures including: (i) dispersion in Eq. [12] was ignored, which yields

$$R^* \frac{\partial C^*}{\partial t} = - V^* \frac{\partial C^*}{\partial x}; \quad [13]$$

(ii) the density of the macromolecule equals the density of the water; (iii) the partition coefficient to the macromolecule's organic C is the same as the partition coefficient to the soil's organic C (K_{oc}), $K_p = K_{oc}$ times the weight fraction of carbon occupied by the macromolecules; (iv) the weight fraction occupied by the organic C (F) is 0.02; (v) the soil partition coefficient can be described by the equation $K_d = 4.47\ F\ K_{ow}^{0.52}$ (Briggs, 1981); (vi) the total porosity (n) of the soil is 0.5; and (vii) the particle density of the soil is 2.65.

The importance of the macromolecule on the mobility of hydrophobic compounds is estimated in Fig. 14–7. If the interstitial velocity of the macromolecule and the water are the same ($V_a = V_o$), the octanol-water partition coefficient vs. the relative chemical mobility (mobility of hydrophobic compounds with macromolecule/mobility without macromolecule) can be presented. A group of chemicals with different K_{ow}'s are shown on the figure for reference purposes only. Figure 14–7 displays the change in mobility of a hydrophobic chemical due to the macromolecules. Macromolecules in the mobile phase can significantly alter the relative mobility of extremely hydrophobic compounds even when the amount of macromolecule is in concentrations typical of groundwater or agricultural soil solution. The importance of the macromolecule rapidly diminishes as the octanol-water partition coefficient of the hydrophobic chemical decreases. At municipal or industrial waste sites where relatively high concentrations of macromolecules might exist, the importance of the macromolecule to chemical mobility could be significant even for chemicals with log K_{ow} of 3 or less. Hydrophilic macromolecules similar to dextran at C concentrations of 100 to 500 mg L^{-1} may change the relative mobility of hydrophobic compounds by an order of magnitude in low C soils.

The significance of differences in interstitial velocities of the two mobile phases are shown in Fig. 14–8. It was assumed, in Fig. 14–8, that the C concentration of the macromolecule was 100 mg L^{-1}. It is possible to plot relative mobility of the macromolecule (V_o/V_a) vs. the relative mobility of the trace compound for different interstitial velocities of the mobile phases. The increased velocity of the macromolecule itself may increase the mobility of hydrophobic trace compounds by a factor of 5 or 10. It can be seen from the figure that if the velocity of the macromolecule drops to 10% of the water velocity, the importance of the macromolecule in accelerating transport approaches zero. Therefore, chemical transport will be facilitated only by macromolecules that are highly mobile. Bengtsson et al. (1987) demonstrated this transport phenomenon experimentally under laboratory conditions.

To summarize and reiterate the main points of the preceding discussion, COC facilitated transport of NOCs will depend primarily on the following: (i) NOCs sorption to COC—will be greatest for low solubility NOCs and

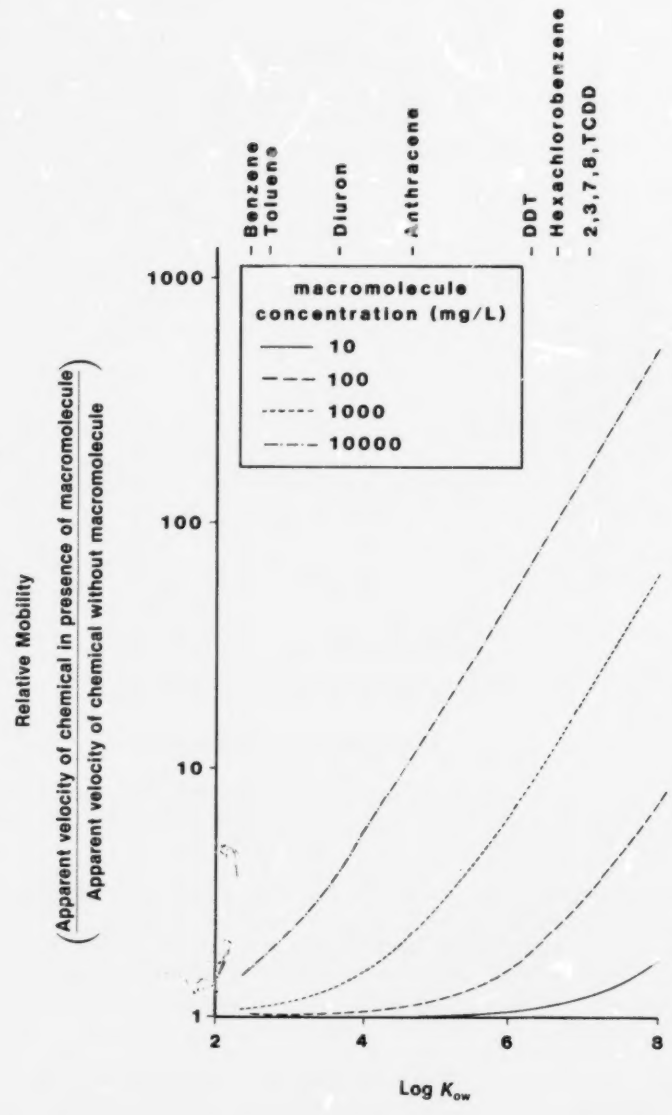

Fig. 14–7. Mobility of a hydrophobic compound relative to the mobility of the same compound without the presence of any COC as a function of octanol-water partition coefficient and amount of organic C in the mobile phase (Enfield & Bengtsson, 1988).

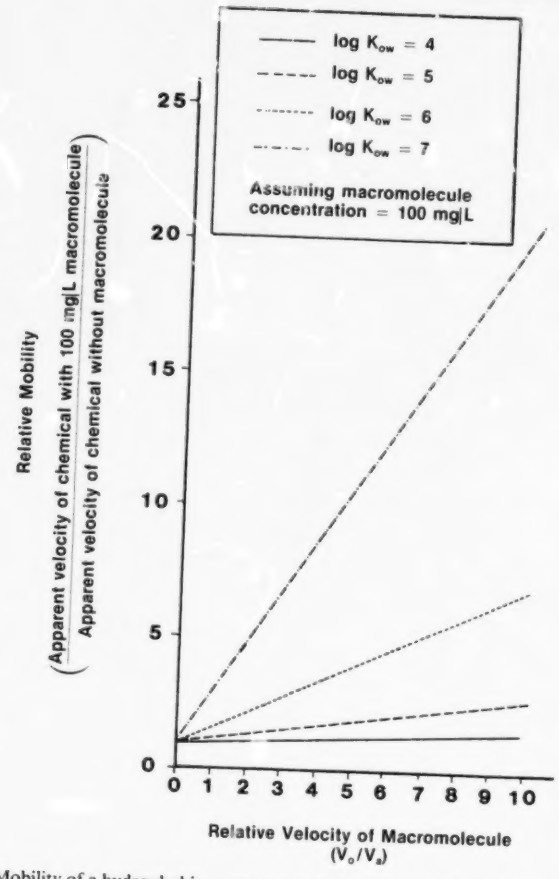

Fig. 14-8. Mobility of a hydrophobic compound relative to the mobility of the same compound without COC vs. the velocity of the COC relative to the velocity of water where the concentration of COC is 100 mg L^{-1} (Enfield & Bengtsson, 1988).

hydrophobic COC; (ii) the amount of COC present in the aqueous phase—at COC concentrations normally observed in nature (5–10 mg L^{-1}) COC facilitated transport of very low solubility NOCs like dioxins and PCBs should be measurable; and (iii) COC mobility—colloid transport through soil has been repeatedly documented in the field and in laboratory soil columns.

14-3 EFFECTS OF RESIDUAL HYDROCARBONS ON THE TRANSPORT OF NEUTRAL ORGANIC COMPOUNDS

Water immiscible fluids are frequently released into the environment as a result of leaking solvent or fuel tanks, leaking transport pipelines, and

improper disposal of oily wastes. The magnitude of the problem may be put in perspective by considering that all of the gasoline storage tanks at gasoline filling stations are potential sources of groundwater contamination. Given the enormity of this potential source of groundwater contamination, it is imperative that immiscible fluid transport and fate be well understood.

Description of immiscible phase transport and solute transport in an immiscible phase is a complex phenomenon dependent on solute, immiscible phase, and porous media characteristics. As an immiscible fluid migrates through the unsaturated zone, a fraction of the fluid, termed the residual saturation, remains behind as coatings on the geologic material or as microdroplets trapped in the pore spaces by interfacial surface tension. The form of residual saturation will depend on which of the fluids is the soil wetting fluid. If the immiscible fluid volume is large enough, the fluid will eventually reach the groundwater where it will either float on top of the water or migrate downward to an impermeable zone depending on its density. As the immiscible fluid migrates through the saturated zone it will displace water from some pores and subsequently a residual saturation will also exist in the saturated zone. Between 15 and 50% of the saturated zone pore space may be occupied by the residual saturation (Felsenthal, 1979; Morrow & Chatzis, 1982).

Whether present as a bulk fluid in the saturated zone, or immobilized as the residual saturation, the immiscible fluid serves as a continuous source term releasing its water soluble and volatile (in the unsaturated zone) components to the aqueous and gas phases. Control of the bulk fluid source may be attained through removal, by pumping, if well placement is close enough to allow adequate interception of the immiscible fluid. However, the fraction of the immiscible fluid constituting the residual saturation is very difficult to remove. Attempts to remove the residual saturation through aqueous phase pumping often leave a significant quantity of immiscible fluid behind (Wilson & Conrad, 1984). The costly, but often only, site remediation option is site excavation of the geologic material and the associated residual saturation.

As the residual saturation of a hydrocarbon fluid weathers, the lighter molecular weight and polar compounds volatilize and dissolve out of the fluid leaving behind a hydrophobic phase even more resistant to removal than the original fluid. In addition to being difficult to remove, these residual hydrocarbons may act as a stationary organic C phase that can sorb NOCs from solution. The following discussion describes a case study where residual hydrocarbons were observed to increase the retardation of NOCs on geologic material.

Spillage of aviation gas at the U.S. Coast Guard installation at Traverse City, MI in 1969 resulted in groundwater contamination. Analysis of core material also indicated the presence of aviation gas residual saturation in the saturated and unsaturated zone. Saturated zone material collected at the site was used in soil columns for solute transport studies. Collection of the sandy saturated zone material and placement in soil columns would have mobilized some of the residual saturation by breaking down the pore structure of the

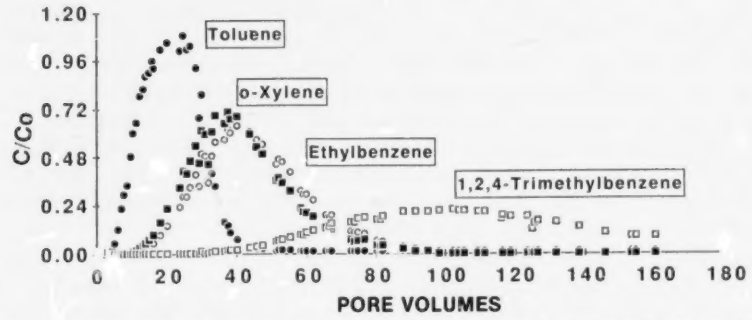

Fig. 14–9. Eluted pulses of four NOCs through saturated zone material contaminated with residual hydrocarbons from aviation gas.

geologic material; however, a fraction of the residual saturation would remain.

Figure 14–9 shows the pulses of four NOCs through a sample of saturated zone material contaminated with the residual hydrocarbons of the aviation gas. The contaminated material was quite sorptive relative to many subsurface geologic materials yielding retardation values of about 20 for toluene. Figure 14–10, however, provides evidence that much of the sorptivity was due to residual hydrocarbons.

Figure 14–10 shows the retardation of a toluene pulse through saturated zone material contaminated with residual hydrocarbons (before solvent flush), and the retardation of a toluene pulse through the same material after the residual hydrocarbons have been removed (after solvent flush) by extraction with organic solvents. It is clear that the toluene pulse was more highly retarded on the material contaminated with the residual hydrocarbons, indicating that these hydrocarbons were providing a hydrophobic environment conducive to the sorption of toluene from solution.

To measure any possible effects of the solvent extraction procedure on the natural sorptivity, i.e., on the natural organic C, of the saturated zone

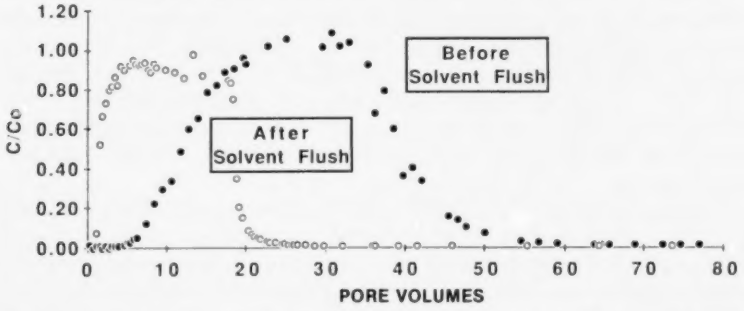

Fig. 14–10. Eluted toluene pulses through saturated zone material contaminated with residual hydrocarbons and through the same material after residual hydrocarbons removal by organic solvent extraction.

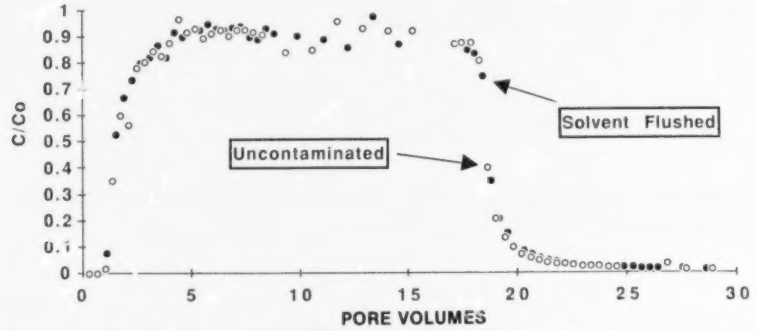

Fig. 14–11. Eluted toluene pulses through solvent extracted saturated zone material and uncontaminated saturated zone material.

material, the retardation of toluene on the solvent washed material was compared to material collected from an uncontaminated area in the saturated zone at Traverse City. Figure 14–11 shows that toluene pulses eluted through both materials were equally retarded, indicating that the changes in sorptivity of the contaminated saturated zone material following solvent extraction were due to residual hydrocarbon removal.

A mathematical description of the process is similar to the discussion presented for the transport of NOCs facilitated by COC except it is assumed that the COC is immobile. The convective dispersive transport is developed in the following equations

$$\frac{\partial(\theta\rho_a C_a)}{\partial t} = D_a \frac{\partial^2(\theta\rho_a C_a)}{\partial x^2} - V_a \frac{\partial(\theta\rho_a C_a)}{\partial x} - K_{ao}\theta\rho_a C_a + K_{oa}\phi\rho_o C_o - K_{as}\theta\rho_a C_a + K_{sa}(1 - n)\rho_s C_s \quad [14]$$

$$\frac{\partial[(1 - n)\rho_s C_s]}{\partial t} = -K_{sa}(1 - n)\rho_s C_s + K_{as}\theta\rho_a C_a \quad [15]$$

$$\frac{\partial(\phi\rho_o C_o)}{\partial t} = -K_{oa}\phi\rho_o C_o + K_{ao}\phi\rho_a C_a. \quad [16]$$

In writing the previous equations, the aqueous phase was assumed to totally cover both the solid phase and the residual organic phase (i.e., the water is the wetting fluid) such that transfer of the contaminant from the residual organic phase to the solid phase requires passage through the aqueous phase. The total change in an elemental volume can be written as the sum of Eq. [14] through [16] or

$$\frac{\partial(\theta\rho_a C_a)}{\partial t} + \frac{\partial(\phi\rho_o C_o)}{\partial t} + \frac{\partial[(1 - n)\rho_s C_s]}{\partial t}$$

$$= D_a \frac{\partial^2(\theta\rho_a C_a)}{\partial x^2} - V_a \frac{\partial(\theta\rho_a C_a)}{\partial x}. \quad [17]$$

When local equilibrium exists, Eq. [17] can be written in terms of the concentration in the aqueous phase as

$$\left(1 + \frac{K_{ao}}{K_{oa}} + \frac{K_{as}}{K_{sa}}\right) \frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial x^2} - V_a \frac{\partial C_a}{\partial x}. \quad [18]$$

By assuming the density of the material retained by the soil as residual saturation to be equal to the density of water, and estimating the volume fraction occupied by residual saturation based on a gas chromatographic analysis of the compounds that could be extracted from the soil referenced to the parent fuel lost in the spill, it is possible to estimate the partition coefficient to the soil and the residual organic phase from NOCs' BTCs. An analysis of this type of data resulted in partition coefficients for toluene, ethyl benzene, o-xylene, and trimethylbenzene. Soil, residual organics, and Jet Fuel no. 4 (JP-4) partition coefficients are given in Table 14-1. The soil partition coefficients along with the standard error of estimates are based on the measured BTCs for the columns after the residual organic material had been removed by solvent extraction. The partition coefficients to the residual organics were estimated assuming the measurements of the volume fraction of the soil occupied by residual organics and the soil-water partition coefficients were correct, and based on BTCs obtained before the residual organic material was removed. The literature values for JP-4 are given only for reference purposes showing that the magnitude is similar to the values obtained in this experiment.

The large partition coefficient to the residual organic material and the potentially large amount of residual material that could be retained in soils and geologic material suggest an explanation for the failure of many cleanup strategies. Pumping water and treating the contaminants on the surface will do little to reduce the magnitude of a groundwater contamination problem when a residual organic material is present.

Table 14-1. Soil and residual organic partition coefficients.

Compound	Soil K_d	Residual organic C	JP-4†
Toluene	0.20 ± 0.02	3 000	2 750
Ethyl benzene	0.30 ± 0.04	13 000	4 780
O-xylene	0.25 ± 0.04	11 000	7 080
Trimethylbenzene	0.54 ± 0.06	42 000	8 910

† Smith et al. (1981).

14-4 CONCLUSION

The preceding discussion underscores the importance of organic C distribution as a determinant of solute transport in the environment. Immobile organic C resulting from sorption of cationic surfactants, or from the existence of residual hydrocarbons, will provide a hydrophobic environment that will enhance NOCs sorption from solution. The result is decreased NOCs mobility in the environment. Conversely, a mobile organic C phase, such as COC dispersed in groundwater, can act as a carrier of hydrophobic NOCs greatly increasing their mobility.

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